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PREPARATION AND PROPERTIES OF BIS(ISOTRITHIONE)BENZOQUNONE, BITBQ AND ITS TTF COMPLEX, $TTF(BITBQ)_{0.90}$

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Abstract Tetrathiapentalenedithione has been combined with benzoquinone to obtain bis-isotrithionebenzoquinone(bitbq; 1,3,5,7-tetrathia-s-indacene-2,6-dithione-4,8-dione). The possible formation of complex with metal or organic donors has been examined. The cyclic voltammogram shows two sets of half-wave oxidation potentials separated to each other by 0.70 V. It can be reduced forming a salt with tetraethylammonium. It forms a non-stoichiometric complex with TTF, $TTF(bitbq)_{0.90}$ by electrochemical oxidation. It was found to have a room temperature conductivity of $(1.9\text{-}0.9)\times10^{-3}$ S/cm along the elongated axis and behave as a semiconductor with variable temperature. It has lattice constants of a= 7.23±0.02 Å, b= 12.50±0.01 Å, c= 10.91±0.01 Å, α= 90.00°, β= 106.34±0.01°, γ= 90.00°, V= 946.05±0.29 Å^3 and belongs to a monoclinic lattice.

INTRODUCTION

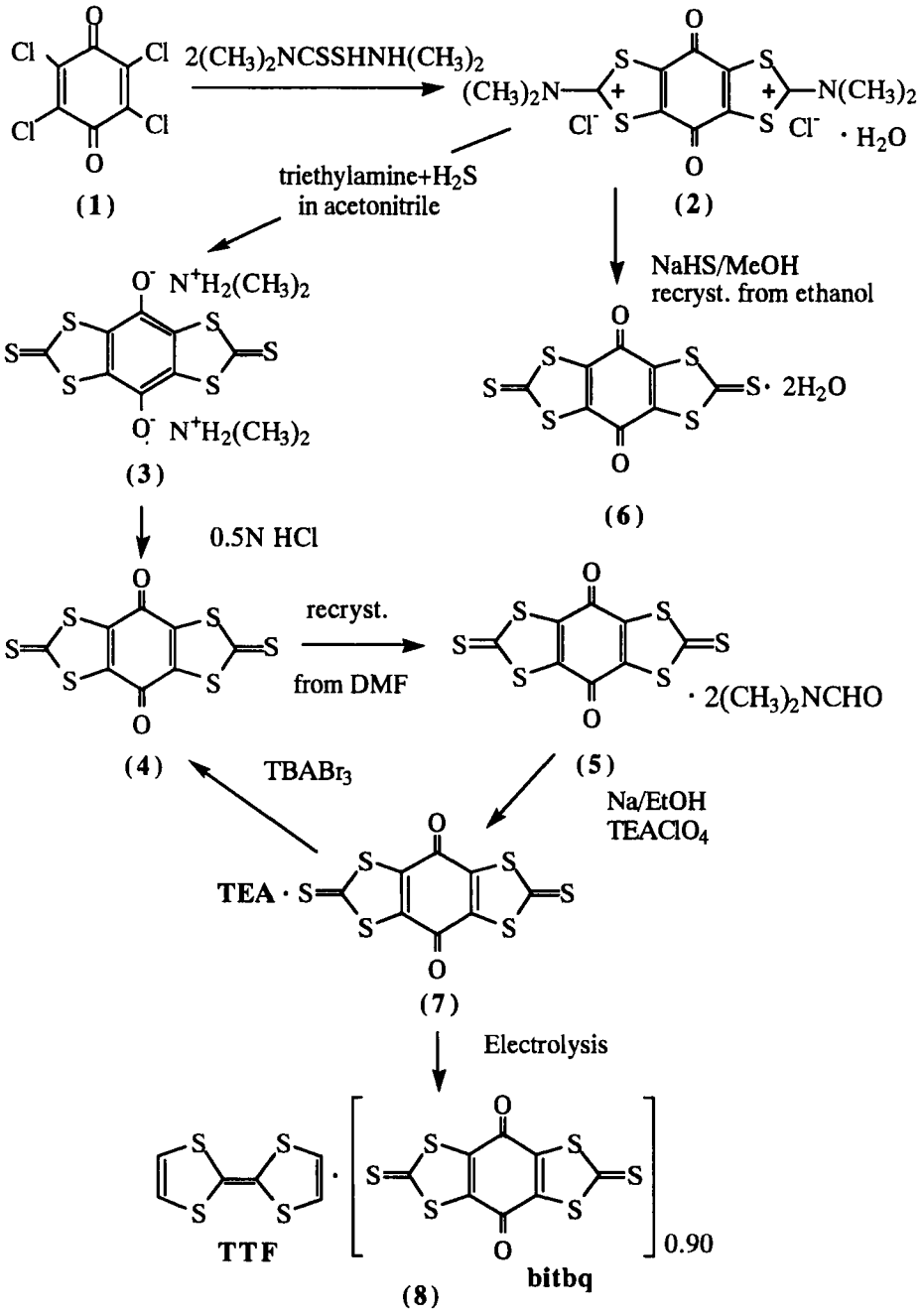
More new metal complexes are currently desired to be prepared for the development and understanding of the electrical conduction behavior, chemical and crystal structures of d-π mixing systems such as metal bisdithiolene conductors exemplified by dmit complexes.[1]

One way to modify the dmit ligand is to replace sulfur atoms in dmit thiocarbonyl by selenium ones to have dmise complexes.[2] Another way of modification of ligand is to expand its π-conjugation system forming dmbit[3,4] or is derivatives.[5] Incorporation of benzene ring into ethylene part of dmit moieties to give metal dmbit has been accompanied by poor crystallinity when it is partially oxidized. To overcome this shortage, bitbq was examined as a ligand precursor for metal complexes. Instead of having metal complex, however, tetraethylammonium salt TEA(bitbq) and a non-stoichiometric complex with TTF, $TTF(bitbq)_{0.90}$ were obtained.

EXPERIMENAL

Bitbq was prepared according to the method reported by Demetriadis et al as following

scheme;[6]



RESULTS

Opening the isotrithione ring of bitbq could not be achieved by sodium metal in ethanol. Neutral bitbq behaves as an electron accepter forming tetraethyl-ammonium salt, TEA(bitbq) (7) when bitbq is treated with $TEAClO_4$ in a basic solution. Its cyclic voltammogram shows two sets of half-wave oxidation potentials separated to each other by 0.70 V as is shown in Figure 1 and Table I.

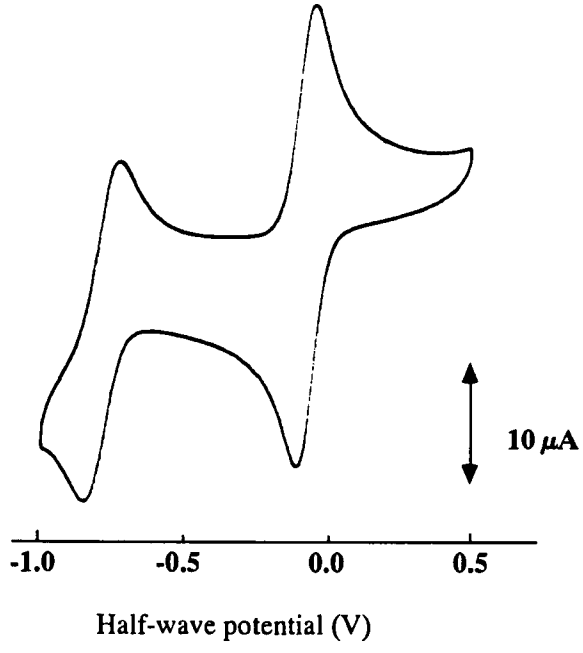


FIGURE 1 Cyclic voltammogram of TEA(bitbq); scan rate of 0.20 V s^{-1}, with Pt working and counter electrodes and an $Ag/AgNO_3$ reference electrode in $1.71x10^{-4}$ mol dm^{-3} acetonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

TABLE I Half-wave oxidation potentials(V) of TEA(bitbq).

$E_{1/2}(1)$	$E_{1/2}(2)$	ΔE
-0.768	-0.069	0.699

This salt can be oxidized by bromine back to a neutral species. When tetraethyl ammonium salt(7) was electrolyzed in acetronitrile with TTF at 2μA, long blue-black needles grow on anode. It was found to have a composition of $TTF(bitbq)_{0.90}$ and lattice constants of a= 7.23±0.02 Å, b= 12.50±0.01Å, c=10.91±0.01 Å, α = 90.00°, β = 106.34 ±0.01°, γ = 90.00°, V= 946.05±0.29 $Å^3$ and to belong to monoclinic lattice. The elongated crystal axis is assigned to a-axis and corresponds twice as long as the averaged

TTF-TTF distance in the stack.

The room temperature conductivity was observed by conventional 4-probe method and was found to be in the range of $(1.9\text{-}0.9)\times10^{-3}$ S/cm. It behaves as an semi-conductor as was revealed by temperature dependent conductivity measurements as illustrated in Figure 2.

DISCUSSION

Isotrithione ring of tetrathiapentalene can be opened to dianion in the strongly basic solution. However, bitbq will not take the ring opening reaction in conventional condition. It would be due to the strong electron-withdrawal effect of quinone part over the isotrithion carbon.

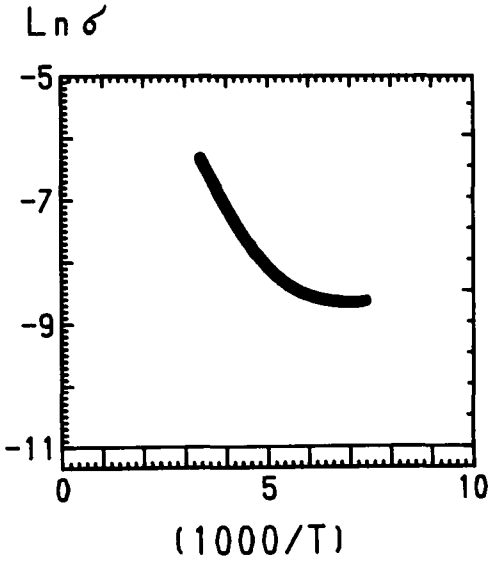


FIGURE 2 Temperature dependence of the conductivity of $TTF(bitbq)_{0.90}$

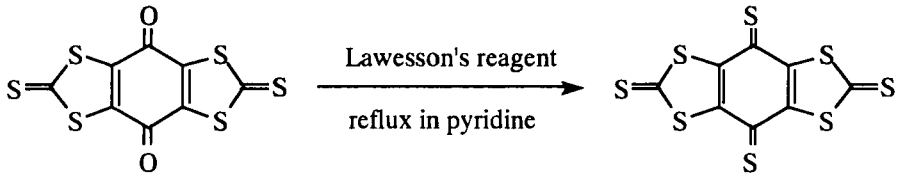
As was revealed from a cyclic voltammogram in Figure 1, bitbq behaves electron acceptor rather than electron donor. Both redox potential waves appear in the lower region than Ag/Ag^+ reference electrode. The lower half-wave potential could be due to electron transfer reaction between dianion and monoanion and the higher one to another electron transfer reaction between monoanion and nuetral species. The potential difference between two half-waves are 0.70 V which is nearly twice as much as that of TTF(0.356V vs Ag/Ag^+ in AN) suggesting a bigger on-site Coulomb repulsion energy over bitbq.

This will partly explain why bitbq does not form 1:1 complex like TTF-TCNQ, but forms nonstoichiometric compound $TTF(bitbq)_{0.90}$ like other TTF salts with halogen. It will also explain why TEA(bitbq) is not partially oxidised by chemical or electrochemical method. The conjugation of quinone part of bitbq would be too strong for the π electrons to spread over the entire molecule.

Room temperature conductivity of $TTF(bitbq)_{0.90}$ is smaller by three or four oder of magnitude than those of other partially oxidised TTF radical salts. The conduction takes place along TTF stacks elongated along *a*-axis where TTF has two fold periodicity with the averaged intrastack distance of 3.61 ± 0.01 Å as was revealed by a preliminary X-ray

structural study.

The following reaction would be more interesting as the next material research;



(4) (9)

The replacement of quinone oxygens in bitbq with sulfur atoms leads to 1,3,5,7-tetrathia-s-indacene-2,4,6,8-tetrathione (9) which would bring a remarkable improvement upon its reactivity, potential complex formation and conduction properties of the derived complexes. These reactions are now under investigation.

Preparation

(2) 1,3,5,7-Tetrathia-s-indacene-2,6-bis(dimethylimmonium)-4,8-dione monohydrate

4.92g of chloranil(1) was suspended in 150ml of methanol-ether(2:1) mixed solvent. 5.44g of dimethylammonium dimethyl-dithiocarbamate in 100ml of methanol was added dropwise under magnetic stirring. The mixture turned to dark brown and was refluxed for 2h. Dark greenish brown mad was separated and dried in vacuo. The product was recrystallized from 100ml of 0.5N HCl solution as golden brown micro crystals. Yield; 2.44g (29.2 %). IR(cm^{-1}); $\nu_{C=O}$: 1595.

(3) Bis(dimethylammonium)-4,8-dioxido-1,3,5,7-tetrathia-s-indacene-2,6-dithione

2g of diimmonium chloride(2) was dispersed in 150ml of acetonitrile and 0.5g of triethylamine was added. Through the reaction mixture, hydrogen sulfide gas was bubbled for 4h at ice temperature. Resultant red product was separated and dried in vacuo one over night. Yield; 1.27g(64.2%). Anal. calc. C(34.93), H(3.91), N(6.79), O(7.75), S(46.62); found C(35.01), H(3.75), N(6.77), O(7.73), S(46.66). UV(nm) 390.0(vs), 337.5(m), 236(s), 200.0(s).

(4) 1,3,5,7-Tetrathia-s-indacene-2,6-dithione-4,8-dione

0.04g of (7) was dissolved in 40ml of hot acetonitrile and 0.05g of tetra-n-butylammonium tribromide in 10ml of acetonitrile was added. The dark brown solution turned light brown. It was cooled to ice temperature for several hours. Black or dark reddish-brown rectangular micro crystals were collected and dried in vacuo. Yield; 0.02g. Anal. calc. C(29.98), S(60.03), O(9.99); found C(29.79), S(60.04), O(10.17).

(5) 1,3,5,7-Tetrathia-s-indacene-2,6-dithione-4,8-dione bis(dimethylaminoform aldehyde)

2g of dioxido(3) was suspended in 50ml of 0.5N hydrochloric acid. Brick red powder

DMF. Yield; 1.47g(64.7%). Anal. calc. C(35.88), H(3.44), N(5.9), S(41.05), O(13.66); found C(36.02), H(3.19), N(5.85), S(40.93), O(14.01)*.
* Determined by the difference.

(6) 1,3,5,7-Tetrathia-s-indacene-2,6-dithione-4,8-dione dihydrate
0.78g of diimmonium(2) was dissolved in 200ml of hot methanol and filtered. 1.57g of NaHS(70% content) was dissolved in 100ml of methanol and was added to the above filtrate. The mixture immediately turned to clear wine red solution. The solution was rot-evaporated to dryness and the solid product was again dissolved in a small amount of hot methanol, filtered and the filtrate was cooled. If no crystallization took place, evaporate the solution gradually and then black shiny needles are to be obtained. Wash with water, dry in vacuo. Anal. calc. C(26.95), H(1.13), O(17.95), S(53.97); found C(27.34), H(0.91), O(17.72), S(54.01). IR(cm^{-1}); $\nu_{C=S}$: 1044, $\nu_{C=C}$: 1410, $\nu_{C=O}$: 1636.

(7) 1,3,5,7-Tetrathia-s-indacene-2,6-dithione-4,8-dione tetraethylammonium
1g of crude product (3) was dissolved in 70ml of hot ethanol and 10ml of dimethylformamide mixed solvent and recrystallized as very long shiny blue-black needles. Yield 0.90g. 0.28g of this crystal was suspended in 50ml ethanol and 0.05g of sodium metal was added and refluxed for 30 minutes under argon bubbling. Soon the reaction mixture turned dark red. Then 0.48g of TBABr in few ml of ethanol was added. The mixture was cooled to ice temperature. Black brown micro crystals were separated, stored in vacuo. Yield; 0.24g. Anal. calc. C(42.64), H(4.43), N(3.11), S(42.68), O(7.10); found C(42.67), H(4.41), N(3.15), S(42.51), O(7.25).

(8) Tetrathiafulvalenium 1,3,5,7-tetrathia-s-indacene-2,6-dithione-4,8-dione, TTF(bitbq)$_{0.90}$
0.10g of tetrathia fulvalen(TTF) and 0.02g of (7) were dissolved in 65ml of acetonitrile. The solution was placed in an H-shaped electrochemical cell with two compartment separated by a glass frit of medium porosity and was electrolyzed galvanostatically at 2μA for two weeks. Long blue black needles were cropped from anode. Typical size of the crystal is 3.4-8.6mm long and 0.03-0.32mm thick. Anal. calc. C(32.18), H(0.82), S(61.16), O(5.84); found C(32.22), H(0.82), S(61.12), O(5.78).

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